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(54) Title: TRANSPARENT LANTHANUM FLUORIDE GLASS–CERAMICS

(57) Abstract

The present invention relates to a transparent glass–ceramic material which includes a glass matrix and a crystalline phase of lanthanum fluoride crystals in the glass matrix, where the transparent glass–ceramic material contains no silica. The present invention further relates to a method of producing the transparent glass–ceramic material.

TRANSPARENT LANTHANUM FLUORIDE GLASS-CERAMICS

FIELD OF THE INVENTION

5   The present invention relates to a transparent
glass-ceramic material and a method of making the
material.

BACKGROUND OF THE INVENTION

10   Recently, transparent materials capable of
efficient frequency upconversion, most being various
rare-earth ion-doped fluoride glasses and crystals, have
received great attention due to the possibilities of
utilizing these materials to achieve blue or green solid
15   state lasers. While no significant difference in
upconversion efficiency is observed between fluoride
glasses and single crystals, single mode optical fiber
doped with a low level of rare-earth ions can be drawn
from fluoride glasses, bringing about highly efficient
20   blue or green upconversion fiber lasers. Unfortunately,
heavy metal fluoride glasses suffer certain undesirable
attributes which have restricted their applications.
Most notably, heavy metal fluoride glasses exhibit poor
resistance to devitrification. U.S. Patent No. 4,674,835
25   to Mimura et al. discusses the crystallization problems
of heavy metal fluoride glasses, one example of which is
called ZBLAN, and the light scattering problems resulting
therefrom.
          The great susceptibility of heavy metal
30   fluoride glasses to devitrification also generates
problems in forming large preforms. Crystallization at

the interface between the core and cladding, during the
production of the preform, causes problems in the most
commonly used methods for preparing an optical fiber.
That is, heavy metal fluoride glasses are quite prone to
5   inhomogeneous nucleation, the consequence of which being
crystallization at the core and cladding interfaces,
particularly during the drawing of the optical fiber.
The resulting fibers are subject to serious scattering
losses due to crystals in the fibers.

10   Devitrification of the heavy metal fluoride
glasses is aggravated when ions necessary to impart
differences in indices of refraction to the core and
cladding are added to the glass composition. Additional
doping, for example, with rare-earth metal ions, also

15   tends to reduce the stability of the glass. As a
consequence of those problems, research has focused on
finding additives which will reduce the tendency of the
glass to devitrify and to increase the chemical stability
thereof. In addition, the preparation of fluoride

20   glasses requires the glass forming components to be
reheated to their softening temperatures, which generally
are about 75 C above the glass transition temperatures.
In addition, fluoride glasses cannot be melted in air but
require a water-free, inert gas environment.

25   Most oxide glasses (such as silica dioxide) are
much more chemically and mechanically stable, are easier
to prepare, and are more easily fabricated into rods,
optical fibers, or planar waveguides than fluoride
glasses. Unfortunately, due to their larger phonon

30   energy, silica glasses are very inefficient for infrared
upconversion. It has also been shown that addition of
oxides into some fluoride glasses improve their
stability, but this is not preferred, since even a small
addition of oxides will significantly quench the

35   upconversion luminescence.

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Early in 1975, Auzel et al., _J. Electrochem. Soc._,
122:101 (1975) reported an interesting class of infrared
("IR") upconversion materials which were prepared from
classical glass forming oxides (SiO_2, GeO_2, P_2O_6, etc. with
PbF_2 and rare-earth oxides), and showed an efficiency
nearly twice as high as LaF_3:Yb:Er phosphor. Since these
kinds of materials were comprised of a mixture of glassy
and crystalline phases, and the embedded crystals were
very large in size (around 10 µm), they were not
transparent.

In Wang et al., "New Transparent Vitroceramics
Codoped With Er^{3+} and Yb^{3+} For Efficient Frequency
Upconversion," _Appl. Phys. Lett._, 63(24):3268-70 (1993),
transparent oxyfluoride vitroceramics (also called glass-
ceramics) containing oxides of large phonon energy, like
SiO_2 and $AlO_{1.5}$, but showing IR to visible upconversion
more efficient than fluoride glass was described. The
composition of Wang contained, expressed in terms of mole
percent,

SiO_2	30	CdF_2	20
$AlO_{1.5}$	15	YbF_3	10
PbF_2	24	ErF_3	1

The glass produced from that composition was
heat treated at 470°C to develop nanoocrystallites which
the authors stated did not reduce the transparency of the
body. The authors posited that the Yb^{3+} and Er^{3+} ions were
preferentially segregated from the precursor glass and
dissolved into the nanocrystals upon heat treatment. The
size of the nanocrystallites was estimated by the authors
to be about 20 nm; that size being so small that light
scattering loss was minimal. The authors reported the
upconversion efficiency of their products to be about 2

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to 10 times as high as that measured on the precursor
glass and other fluoride-containing glasses. However,
the crystals which are formed in the Wang glass have a
cubic lattice structure and this limits the concentration
of some of the trivalent rare-earth elements which may be
incorporated into the crystal phase. Another problem
with these materials is that they require cadmium in the
formulation. Cadmium is a carcinogen and, thus, its use
is restricted. Hence this type of glass would not be
desirable for any large scale manufacturing operation.

The present invention is directed toward
overcoming these above-noted deficiencies.

SUMMARY OF THE INVENTION

The present invention relates to a transparent
glass-ceramic material which includes a glass matrix and
a crystalline phase of lanthanum fluoride crystals in the
glass matrix, where the transparent glass-ceramic
material does not contain silica.

Another aspect of the present invention relates
to a method of making a transparent glass-ceramic
material which includes providing a glass matrix and
treating the glass matrix under conditions effective to
produce the transparent glass-ceramic material which
includes a glass matrix and a crystalline phase of
lanthanum fluoride crystals in the glass matrix, where
the transparent glass-ceramic material does not contain
silica.

Transparent glasses containing crystals are
highly desirable in applications where there is a
requirement for the glass to be easily melted or formed
and additionally to contain a crystal, where the crystal
itself may be difficult or expensive to synthesize. Such
transparent glasses, containing lanthanum fluoride
crystals, are especially desirable where the crystal
itself provides highly desirable features, such as

optical activity. In addition, the glass-ceramics of the present invention are easily produced and can be melted at low temperature relative to many silicate glasses, in air. Further, lanthanum fluoride has the particular

5   advantage of being able to accommodate large concentration of any rare-earth element into its crystal structure and is not a carcinogen.

BRIEF DESCRIPTION OF THE DRAWINGS

10   Figure 1 is a graph comparing the emission spectra of a glass-ceramic of the present invention with a fluoride glass at 1550 nm.

Figure 2 is an X-ray diffraction pattern of a

15   precursor glass of the present invention.

Figure 3 is an X-ray diffraction pattern of a glass-ceramic of the present invention.

Figure 4 is a Differential Thermal Analysis ("DTA") curve showing the position of the glass

20   transition temperature (Tg) and the crystallization temperature required to produce a glass-ceramic of the present invention.

Figure 5 is a diagram showing the optimum region for forming a glass-ceramic of the present

25   invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a transparent

30   glass-ceramic material which includes a glass matrix and a crystalline phase of lanthanum fluoride crystals in the glass matrix, where the transparent glass-ceramic material does not contain silica.

Another aspect of the present invention relates

35   to a method of making a transparent glass-ceramic material, which includes providing a glass matrix and treating the glass matrix under conditions effective to

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produce the transparent glass-ceramic material, which
includes a glass matrix and a crystalline phase of
lanthanum fluoride crystals in the transparent glass-
ceramic material, where the glass-ceramic material does
5   not contain silica.

Preferably, the transparent glass-ceramic
materials include lanthanum fluoride crystals having
uniform size distribution and interpartical separations
of the order of 10-40 nanometers. Further, it is
10   preferable for the size of each crystal of the
crystalline phase to be in the range of about 5-15
nanometers. Further, the glass-ceramic material of the
present invention preferably contains from about 5% to
about 30% by volume crystals. Thus, an "ultra-
15   transparent" glass-ceramic is produced, which is useful
for doping with active rare-earth elements. "Ultra-
transparent" signifies that the glass-ceramic material of
the present invention, when doped with active rare-earth
elements, has optical scattering properties which are
20   indistinguishable from a glass, in particular, having
minimal light scattering loss.

It is desirable for the transparent glass-
ceramic composition to include 45 to 55 wt.% LaF , 20-25
wt.% B_2O_3, 10-20 wt.% Al_2O_3, and 10-15 wt.% BaF_2.
25   Optionally, the composition may also include 0-15 wt.%
PbF_2, 0-10 wt% Y_2O_3 and 0-10 wt.% Ta_2O_5.

In addition, the transparent glass composition
may include fluorides or oxides of one or more rare-earth
elements other than lanthanum. Preferably, the
30   composition includes from 0 - 5 wt. % fluorides or oxides
of these additional rare-earth elements. The additional
rare-earth elements are Y, Ce, Pr, Nd, Pm, Sm, Eu, Gd,
Tb, Dy, Ho, Er, Tm, Yb, and Lu.

The rare-earth elements may be contained
35   entirely in the crystalline phase. Alternatively, the
rare-earth elements are contained both in the glass
matrix and in the crystalline phase.

The transparent glass-ceramic material is produced by providing a glass matrix and treating the glass matrix under conditions effective to produce the transparent glass-ceramic material, which includes a

5   glass matrix and a crystalline phase of lanthanum fluoride crystals in the glass matrix, wherein the glass-ceramic material does not contain silica.

Optionally, the glass matrix is provided as a formed glass shape. Alternatively, the glass matrix is

10 provided by producing the glass matrix. The glass matrix is produced by any traditional glass making procedure. For example, glass components which include alkoxides and are formulated to produce a glass matrix having the desired composition are used in a sol gel approach, such

15 as disclosed in U.S. Patent No. 5,494,863 to Mathur, which is hereby incorporated by reference, to produce the glass matrix. In addition, for example, the glass matrix may be produced using chemical vapor deposition techniques.

20 A particularly preferred way of providing the glass matrix is by producing the glass matrix through traditional melting and forming techniques. Preferably, the glass matrix is produced by first melting together batch components calculated to produce a glass matrix

25 having the desired composition to give a glass melt. Importantly, no silica is utilized. Preferably, the glass components are melted at temperatures from about 1000 C to about 1200 C for from about .25 to about 2 hours. Next, the glass melt is formed into a glass

30 shape. Suitable forming procedures include rolling, pressing, casting, or fiber drawing. The glass shape is then preferably a patty, rod, sheet, or fiber.

Subsequently, the glass matrix provided is treated under conditions effective to produce a transparent

35 glass-ceramic material having a glass matrix and a

crystalline phase of lanthanum fluoride crystals in the
glass matrix.

Preferably, the treating step is achieved by
heating the glass matrix to ceram the glass matrix.   The
5   heating step is designed to promote phase separation and
crystallization of the lanthanum fluoride phase,
producing a glass-ceramic material which includes a
crystalline phase of lanthanum fluoride in a glass
matrix. Preferably, the glass matrix is heated in a
10   heating step at a temperature from about 600°C to about

700°C. The exact heat treatment temperature is determined
by the crystallization behavior of the lanthanum fluoride
phase, which can be determined by differential thermal
analysis. The glass matrix is then cooled to room
15   temperature. Perferably, the article is rapidly cooled
to the anneal temperatures (about 560°C), then cooling
proceeds at a rate sufficient to remove residual
stresses.

The transparent glass-ceramic material is
20   especially useful where a glass matrix, which is easily
melted or easily formed, is desired or where the glass
matrix contains a crystalline phase which may be
difficult or expensive to produce.

Further, a transparent glass-ceramic material
25   which includes lanthanum fluoride crystals in the glass
matrix, is especially useful where the crystals act as
selective hosts for other rare-earth elements. A
dramatic change is observed in the emission spectra of
ErF_3 doped lanthanum fluoride glasses after ceramming,
30   indicating significant partitioning of the rare-earth
element into the crystal phase.

It is not necessary to have complete
partitioning of the rare-earth element into the
crystalline phase. For certain applications, such as
35   gain-flattened amplifiers, for example, a combination of
Er^{3+} in the glass matrix and in the crystalline phase may

be optimal. This permits tailoring of the site sizes and geometries of the lanthanum fluoride crystals to optimize the local environments of any dopant lanthanide ions.

<u>EXAMPLES</u>

5   <u>Example 1</u>

Various precursor glass materials were produced as follows. Glass forming batch materials calculated to produce the desired compositions were mixed, and the mixture was melted in covered platinum crucibles for 1-

10   2 hours at 1200°C in air to produce a glass melt. The glass melt then was cast to produce a precursor glass.

Examples of representative precursor glass compositions obtained are listed in Table 1 below. Precursor glasses having the appearance of clear glass

15   are desirable for ceramming to produce the transparent glass-ceramic compositions of the present invention.

Thus, compositions 1-3, 7, 11, 18, 21, 27-30, 34, 35, 41, and 42 are desirable precursor glasses. Figure 5 illustrates an optimum region for forming

20   desirable precursor glasses.

Table 1

ID	La₂O₃	LaF₃	B₂O₃	PbF₂	PbO	Al₂O₃	Y₂O₃	ZnF₂	BPO₄	BaF₂	SiO₂	Tb₄O₇	Appearance
1	50		25									25	clear glass
2	37.5	12.5	25									25	clear glass
3	12.5	37.5	25									25	clear glass
4		50	25									25	crystals/glass
5		50	25		25							25	crystals/glass
6		40	25		25								devitrified
7		40	25		25	10					10		clear glass
8		50	20	10									phase separated
9		50	20		25	5					10		devitrified
10		50	25		15	10							hazy glass
11		50	25		10	15							clear glass
12		50	25			25							didn't melt
13		50	25		5	15		5					crystals glass
14		50	25		5	20		5					didn't melt
15		50	25			15		10					partly melted
16		50	20		15	15							surface crystals/glass
17		50	15		25	10							devitrified
18		50	25	5	5	15							clear glass
19		50	25	10		15							devitrified
20		45	25	10		15							5 ErF₃ clear glass
21		50	25	10		15							clear glass

ID	La₂O₃	LaF₃	B₂O₃	PbF₂	PbO	Al₂O₃	Y₂O₃	ZnF₂	BPO₄	BaF₂	SiO₂	Ta₂O₅	Appearance
22		50		10		15			25				didn't melt
23		50	25	10		7.5	7.5						surface devit
24		50	20	15		7.5	7.5						devitrified
25		50	25			7.5	7.5	10					devitrified
26		50	20	10		15			5				devitrified
27		50	25	10		10				5			clear glass
28		50	25	10		5				10			clear glass
29		50	25	5		10				10			clear glass
30		50	25			10				15			clear glass
31		50	20			10				15			clear glass
32		50	20			10				20	5		surface devit.
33		50	22.5			15				10			2.5 AgF, devit.
34		50	25			10				15			clear glass
35		50	25			10				15			clear glass
36		50	22.5			17.5	5			10			few crystals
37		50	22.5			12.5	7.5			10			clear glass
38		50	20			12.5	5			10			surface devit.
39		50	22.5			10	5			10			2.5 A₂F₃, s. crystals
40		50	22.5			5	5			12.5			5 AlF₃, s. crystals
41		50	20			10	5			10		5	clear glass
42		50	15			10	5			10		10	clear glass

Example 2

A transparent glass-ceramic material with lanthanum fluoride crystals having a composition as shown in Table 2 below was prepared by first preparing the precursor glass as described in Example 1. The precursor glass then was cerammed at 680°C to produce a transparent glass-ceramic material.

Table 2

LaF_3	47.5 wt. %
B_2O_3	25 wt. %
PbF_2	10 wt. %
Al_2O_3	15 wt. %
Er_2O_3	2.5 wt. %

A comparison of the emission spectra of this sample (line 1) versus the emission spectra of a pure fluoride glass (line 2) at 1550 nm is shown in Figure 1. Importantly, the transparent glass-ceramic has a long, very flat plateau, extending to 1560 nm, indicating that this material is useful as an amplifier host, because of the uniform gain in this area.

Example 3

A transparent glass-ceramic having lanthanum fluoride crystals having a composition shown in Table 3 below was prepared as described in Example 2.

Table 3

LaF$_3$	50 wt. %
B$_2$O$_3$	20 wt. %
Al$_2$O$_3$	10 wt. %
PbO	20 wt. %

As shown in Figure 2, after melting and before ceramming, X-ray diffraction indicates that the precursor material
5   was a glass, with no crystalline phase present. As shown in Figure 3, after ceramming, a glass-ceramic was present, having a crystalline LaF$_3$ phase.

Example 4
10   A transparent glass-ceramic having lanthanum fluoride crystals having a composition shown in Table 4 below was prepared.

Table 4

LaF$_3$	50 wt.%
B$_2$O$_3$	25 wt.%
Al$_2$O$_3$	15 wt.%
PbF$_2$	10 wt.%

15

As shown in Figure 4, a Differential Thermal Curve indicates the glass transition temperature (Tg) of about 550°C for the composition and the ceramming temperature (Tc) of approximately 700°C. Specifically,
20   the onset Tg was 567°C, with a midpoint of 575°C. At a temperature of approximately 890°C, additional undesirable crystallization occurs, indicating that lower ceramming

temperatures are necessary to produce the glass-ceramic material of the present invention.

The optimum region for forming a four component system of the inventive glass-ceramic is shown in Figure 5. In this model, the glass ceramic is comprised of 50 wt.% LaF_3, and 50 wt.% ($B_2O_3+BaF_2+Al_2O_3$). The region indicated in Figure 5 represents the optimum region for components B_2O_3, BaF_2 and Al_2O_3.

Although the invention has been described in detail for the purpose of illustration, it is understood that such detail is solely for that purpose, and variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention which is defined by the following claims.

15

WHAT IS CLAIMED:

     1   A transparent glass-ceramic material
comprising:

          a glass matrix and

          a crystalline phase of lanthanum fluoride
crystals in the glass matrix, wherein the transparent
glass-ceramic material contains no silica.

     2   The transparent glass-ceramic material
according to claim 1, wherein the lanthanum fluoride
crystals have a uniform size distribution.

     3   The transparent glass-ceramic material
according to claim 2, wherein the lanthanum fluoride
crystals have a size of no greater than about 15
nanometers.

     4   The transparent glass-ceramic material
according to claim 1, wherein the transparent glass-
ceramic material comprises: 45 to 55 wt. % LaF_3, 20 - 25
wt. % B_2O_3, 10 - 20 wt. % Al_2O_3, and 10 - 15 wt. % BaF_2.

     5   The transparent glass-ceramic material
according to claim 4 further comprising: 0 - 15 wt. %
PbF_2, 0 - 10 wt. % Y_2O_3 and 0 - 10 wt. % Ta_2O_5.

     6   The transparent glass-ceramic material
according to claim 4, further comprising:

          up to 5 wt. % fluorides or oxides of one
or more additional rare-earth elements.

     7   The transparent glass-ceramic material
according to claim 6, wherein the additional rare-earth
elements are selected from the group consisting of Y, Ce,
Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu.

8   The transparent glass-ceramic material
according to claim 7, wherein the additional rare-earth
elements are contained entirely in the crystalline phase.

5   9   The transparent glass-ceramic material
according to claim 7, wherein the additional rare-earth
elements are contained both in the glass matrix and in
the crystalline phase.

10   10   A method of making a transparent glass-
ceramic material comprising:
                 providing a glass matrix and
                 treating the glass matrix under conditions
effective to produce the transparent glass-ceramic
15 material comprising a glass matrix and a crystalline
phase of lanthanum fluoride crystals in the glass matrix,
wherein the transparent glass-ceramic material contains
no silica.

20   11   The method according to claim 10, wherein
the transparent glass-ceramic material comprises: 45 to
55 wt.% LaF, 20-25 wt.% B_2O , 10-20 wt.% Al_2O , and 10-15
wt.% BaF_2.

25   12   The method according to claim 11, wherein
the transparent glass-ceramic material further
comprises:0-15 wt. % PbF_2,0-10 wt.% Y_2O_3 and 0-10 wt.%
Ta_2O_5.

30   13   The method according to claim 11, wherein
the transparent glass-ceramic material further comprises:
                 up to 5 wt.% fluorides or oxides of one or
more additional rare-earth elements.

35   14   The method according to claim 13, wherein
the additional rare-earth elements are selected from the

group consisting of Y, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu.

15   The method according to claim 14, wherein the additional rare-earth elements are contained entirely in the crystalline phase.

16   The method according to claim 14, wherein the additional rare-earth elements are contained both in the crystalline phase and in the glass matrix.

17   The method according to claim 10, wherein the providing comprises:

        melting the glass matrix to produce a glass melt and

        forming the glass melt into a glass shape.

18   The method according to claim 17, wherein the melting is performed at temperatures from about 1000° C to about 1200°C for about .25 to 2 hours.

19   The method according to claim 10, wherein the treating comprises:

        heating the glass matrix to form the transparent glass-ceramic material comprising a crystalline phase of lanthanum fluoride crystals in the glass matrix.
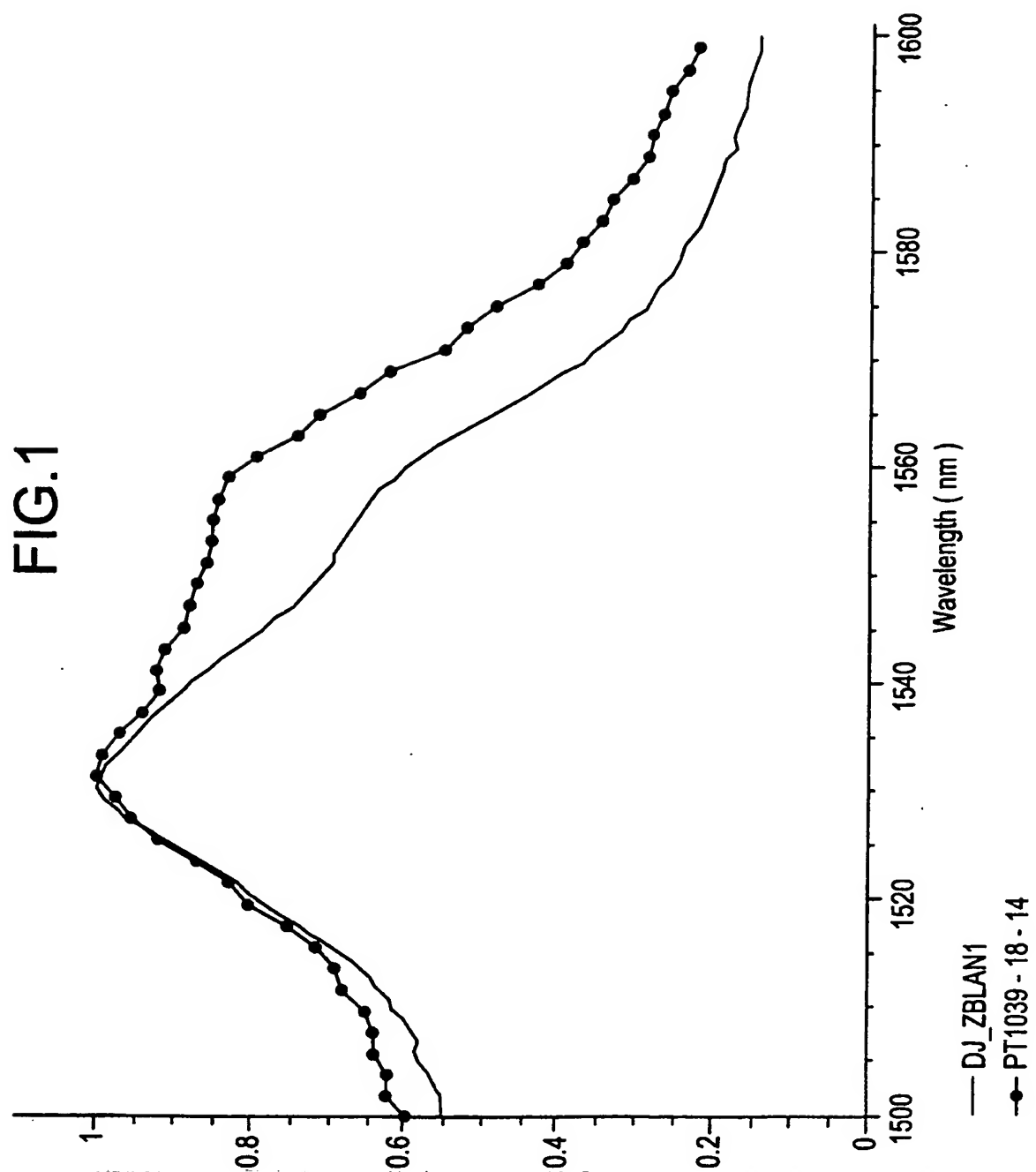
20   The method according to claim 19, wherein the heating comprises:

        heating the glass matrix at a temperature from about 600°C to about 700°C.

21   A product prepared by the method according to claim 10.

22   A product prepared by the method according to claim 17.
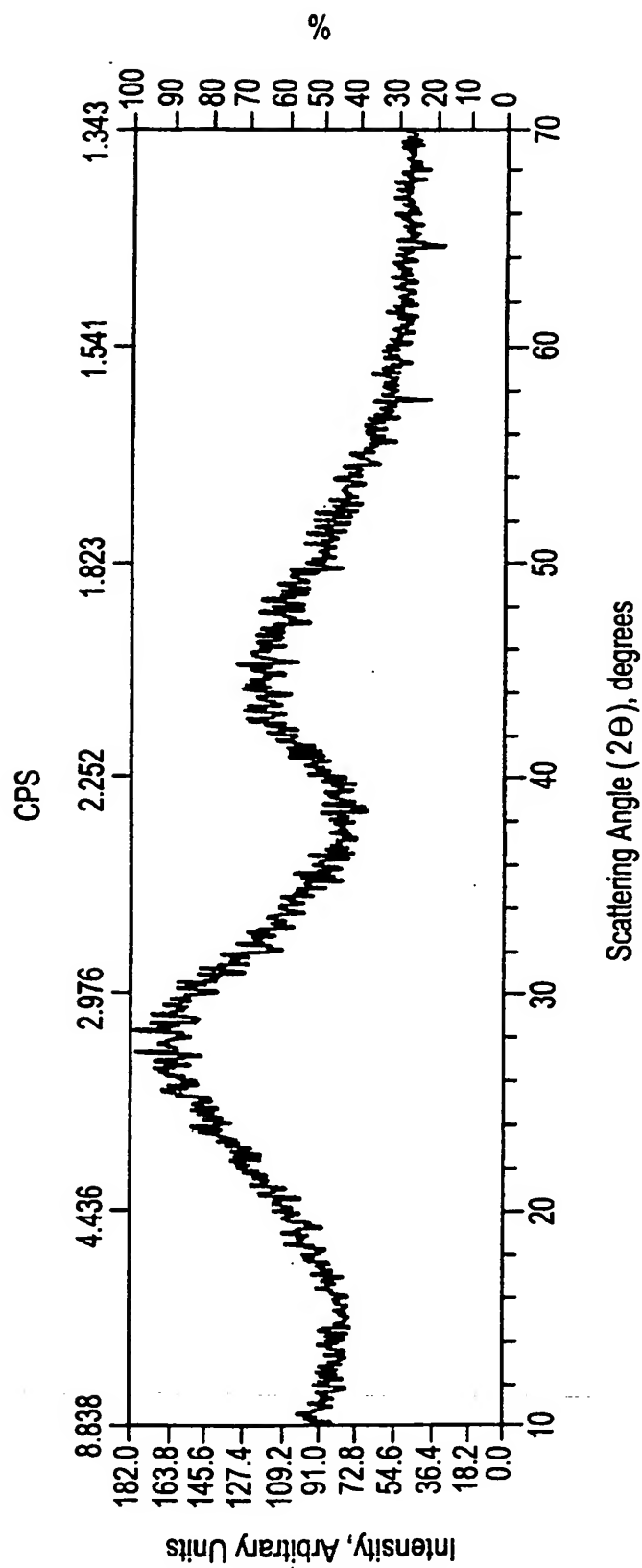
23   A product prepared by the method according
5   to claim 20.

FIG.1

FIG.2

FIG.3A

LANTHANUM FLUORIDE / FLUOCERITE - (LA), SYN

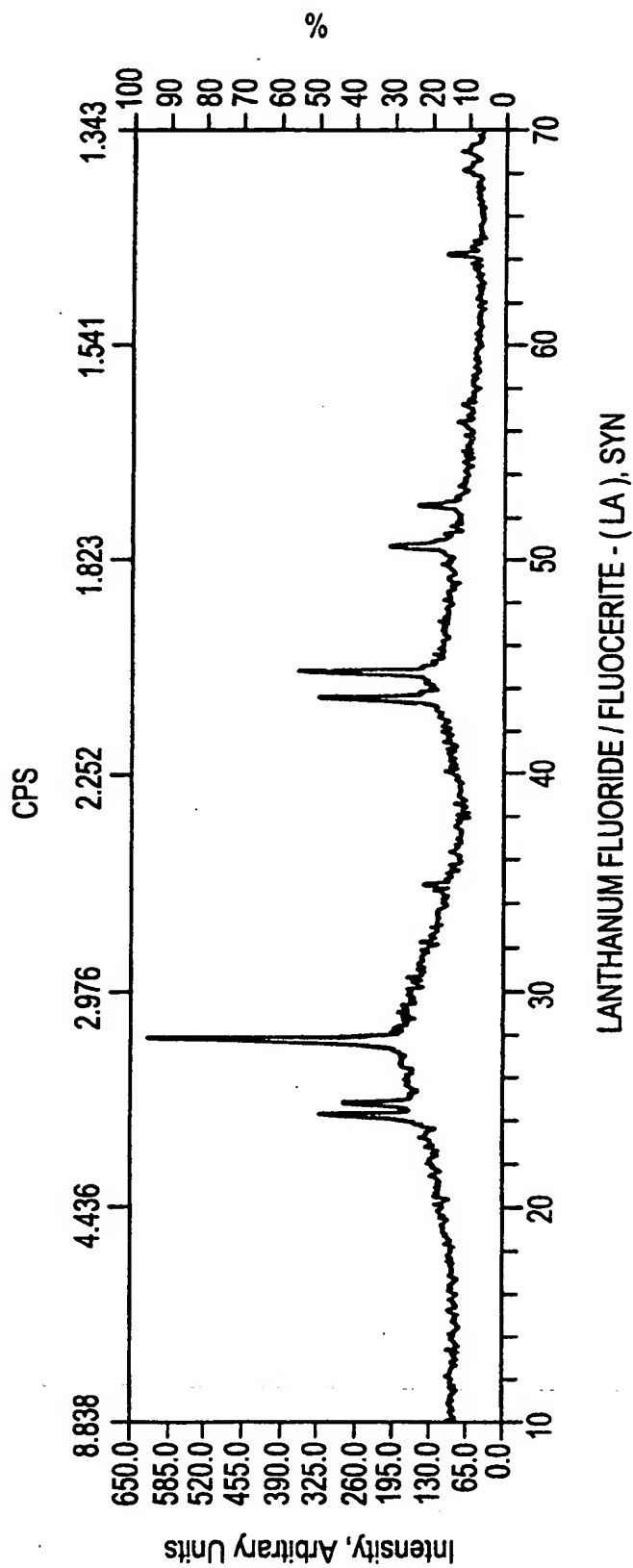# FIG.3B
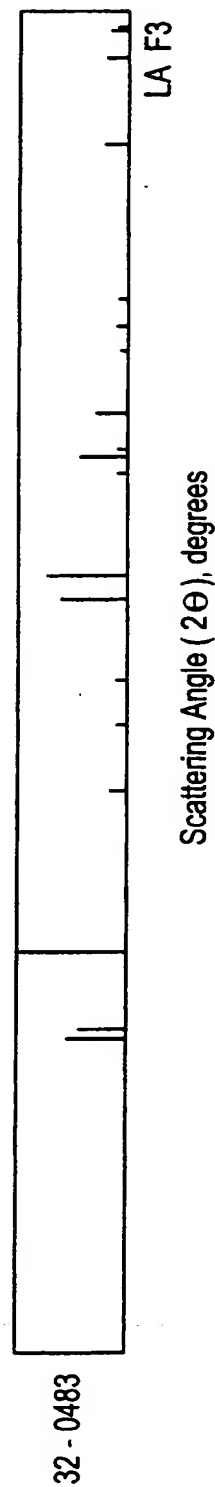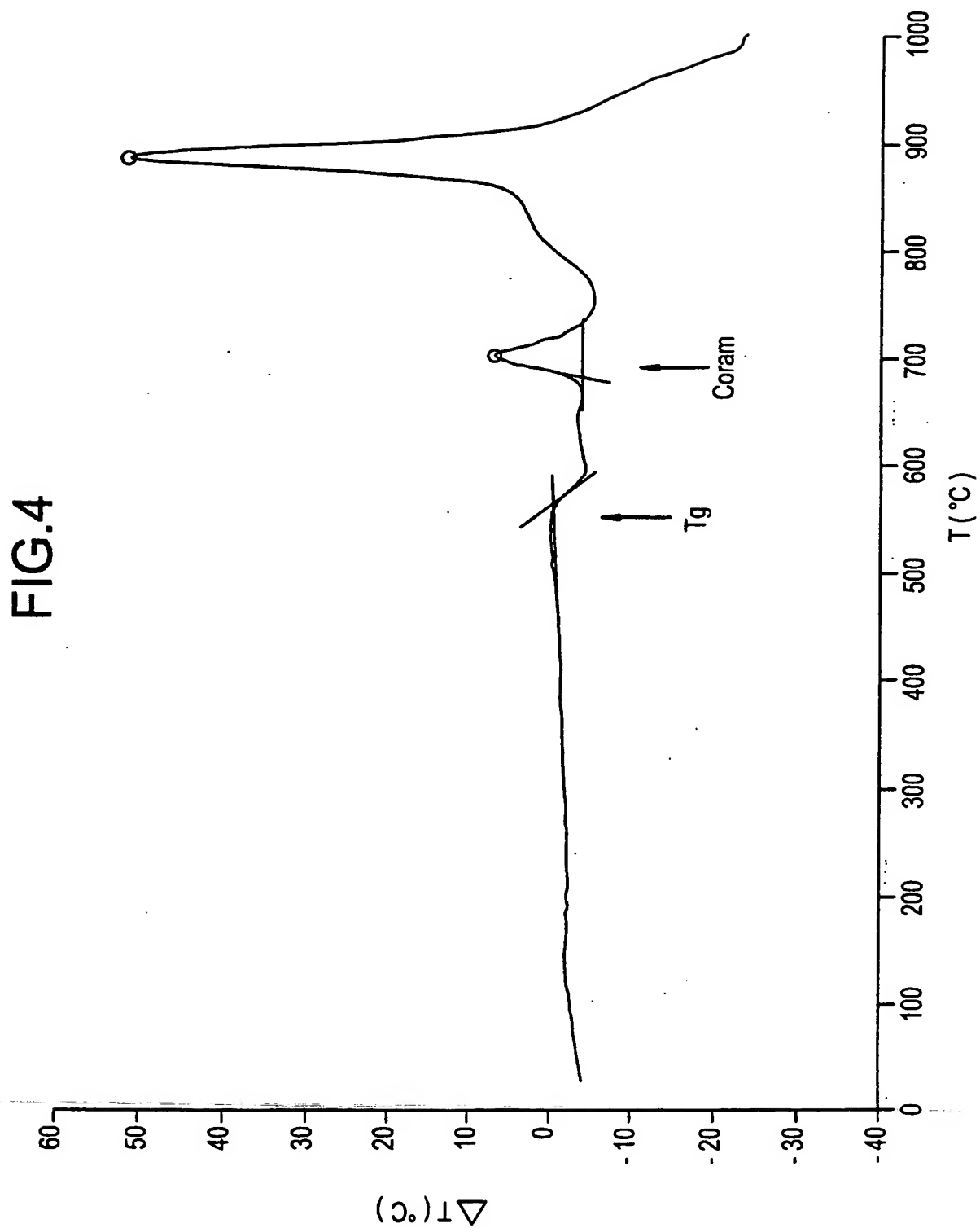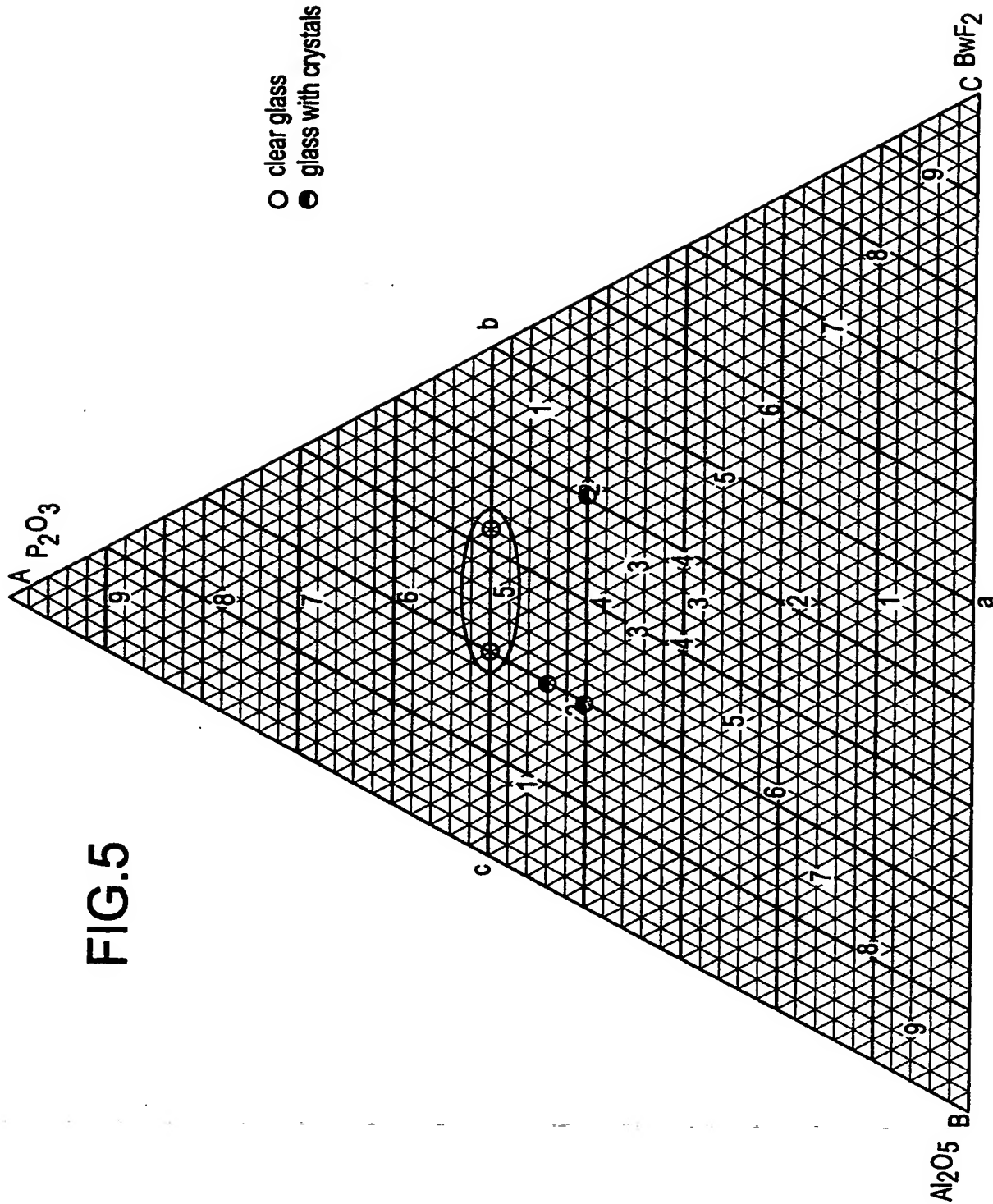

32 - 0483

LA F3

Scattering Angle (2Θ), degrees

FIG.4

FIG.5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/12262

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :CO3C 10/16, 3/247
US CL :501/3,44,50,51; 65/33.3

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 501/3,44,50

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,032,351 A (AUZEL et al) 28 June 1977, col. 3, lines 22-37.	1,210,17,19,21-23
A	US 5,545,595 A (WANG et al) 13 August 1996.	1-23
A	US 5,420,080 A (WANG et al) 30 May 1995.	1-23

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	
"A"	document defining the general state of the art which is not considered to be of particular relevance	
"E"	earlier document published on or after the international filing date	
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"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search	Date of mailing of the international search report
03 SEPTEMBER 1998	16 OCT 1998

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